



SIZE-STRAIN X-RAY LINE PROFILE ANALYSIS AND CRYSTALLITE SIZE DISTRIBUTION OF NANOSTRUCTURED ZnO

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ABSTRACT

The Warren-Averbach (W-A) method is considered the most rigorous Line Profile Analysis (LPA) methodology for the determination of mean crystallite sizes and microstrains from X-ray diffraction measurements. For all LPA methods it is necessary to correct the measured line breadth from the instrumental contribution and, as the calculations in W-A method are performed in Fourier space, this correction can be made as the deconvolution of the instrumental from the experimental breadths by the called Stokes method. In this work a computer program is developed to perform the Discrete Fourier Transform on XRD data and to apply the Stokes deconvolution. To test and validate the program, powder diffraction data for a CeO₂ sample, used in a Round-Robin collective work, were processed and compared to the Round-Robin results published. The results obtained for the mean crystallite sizes were compatible with the values established in the reference work. Finally, the methodology was applied in nanostructured ZnO synthesized in different reaction temperatures (50°C, 70°C and 90°C) to evaluate its mean crystallite size, microstrain and the crystallite size distribution.

Keywords: Warren-Averbach, standard material, instrumental correction, crystallite size distribution.

1. INTRODUCTION

Zinc oxide's (ZnO) physical and chemical properties make it a viable and extremely attractive compound to use in a variety of nanotechnology applications. Some of these applications include biomedical, energy, sensors, and optics. For example it has single crystal-growth technology applications and offers significantly lower fabrication costs when compared to other semiconductors used in nanotechnology [1]. One of the earliest publication regarding zinc oxides dates from 1945 [2] and the attention on this compound increased during the 1950s and 1970s due to its unique characteristics related to growth, doping, transport, band-structure, and luminescence. The popularity of zinc oxides is increasing again due to its potential for epitaxial layer growth, quantum wells, and nanostructures.

Zinc oxide has a stable wurtzite structure with lattice spacing $a = 0.325$ nm and $c = 0.521$ nm and is a II-VI semiconductor with a large bandgap ($E_g = 3.37$ eV) and high exciton binding (60 meV). The understanding of its crystallographic properties is very important to expand its applications in several areas. For that purpose, the microstructure of nanostructured ZnO was studied by means of X-ray line profile analysis such as the Warren-Averbach method.

The mean crystallite sizes and microstrains due to defects in the crystal structure can be determined by X-ray line profile (XLPA) methods. The use of XLPA methods has been

largely applied due to its simplicity in sample preparation, data acquisition and capacity to analyze a large volume of the material, providing better statistical results. For a more elaborated analysis, the Warren-Averbach (W-A) method [3] is considered the most rigorous Line Profile Analysis (LPA) methodology for the determination of mean crystallite sizes and microstrains from diffraction measurements. In this work a computer program was developed to speed up the application of the W-A method. To validate the program powder diffraction data for a CeO₂ sample, used in a Round-Robin collective work [4], were analyzed and compared to the Round-Robin results published. It was possible to verify that the results obtained with the program are in agreement with the results on the reference. After the validation of the program, the methodology was applied calculate the mean crystallite size of nanostructured ZnO samples. It is also shown that is possible to determine the crystallite size distribution of the material assuming spherical morphology of the crystallites and the lognormal distribution.

2. EXPERIMENTAL

Three samples of nanostructured ZnO synthesized at different reaction temperatures of 50°C, 70°C and 90°C were analyzed [5]. To perform the instrumental correction a Y₂O₃ standard reference material (SRM) produced at IPEN [6] was used. This SRM was studied by Martinez et al. [7] using synchrotron radiation and it was certified as a proper material

to be used in size-strain analysis to correct the instrumental contribution in X-ray profiles.

3. METHODS

3.1. Computer program development

A computer program that performs the Discrete Fourier Transform (DFT) was devised in Python programming language. Prior to apply the DFT, a series of treatment on the diffraction peak data can be necessary. The first treatment consists in a peak smoothing if the data statistics is not adequate. The smoothing is performed utilizing the Savitzky-Golay [8] algorithm or a method of adjacent points considering 3, 5 or 7 points successively [9,10]. However it must be pointed out that the smoothing can be used only in cases where the peak does not present ideal conditions (low counting time or for low intensity reflections, which may cause noisy data), since its use can affect the peak shape. For the background correction a simple linear regression is performed on the “tails” on both sides of the peak. At this point the Lorentz-Polarization correction is performed to take into account the scattering of non-polarized wave [11]. The final steps are the centralization and normalization of the peak as required by the DFT algorithm. Then the DFT can finally be executed. The Stokes method [12] is applied in order to correct the instrumental breadth by deconvoluting the SRM measured peaks from the sample’s measured peaks. The software was validated analyzing a dataset provided in a size-strain analysis of a Round-Robin CeO₂ sample [4].

3.2. Warren-Averbach method

Warren and Averbach [3] showed that size and strain contributions are convoluted in the profile of a Bragg reflection. Since the X-ray diffraction profile can be represented as a Fourier series in the reciprocal space, its real coefficient can be written as:

$$A\left(L, \frac{1}{d}\right) = A^S(L)A^D\left(L, \frac{1}{d}\right) \quad (1)$$

Where L is the Fourier length and d the interplanar spacing. The method proposed by Warren and Averbach permits to separate these two contributions considering Eq. 2:

$$\ln A\left(L, \frac{1}{d}\right) = \ln A^S(L) - 2\pi^2\langle\varepsilon_L^2\rangle L^2/d^2 \quad (2)$$

Where $A^S(L)$ is the Fourier coefficient related to the size and $\langle\varepsilon_L^2\rangle$ is the mean square strain related to L and can be used to calculate the root mean square strain ($\sqrt{\langle\varepsilon_L^2\rangle}$, RMSS) which is more used.

Eq. 2 was plotted for d^{-2} corresponding to the (101) and (202) reflections of the ZnO samples. This procedure allows separating the size from the linear coefficients and microstrain from the slopes of the linear regressions. Finally, to calculate the mean crystallite sizes, the values of $A^S(L)$ against L were plotted and the intercept of the linear regression on the region for small L in the L -axis gives the area-weighted mean crystallite size ($\langle L \rangle_A$) [8].

3.3. Crystallite size distribution

The crystallite size distribution can be described by analytical functions. A function that is widely applicable in several areas in materials science to describe volumetric entities is the lognormal function [8]:

$$g(D) = \frac{1}{\sqrt{2\pi}D\ln\sigma} \exp\left\{-\frac{1}{2}\left[\frac{\ln(D/D_0)}{\ln\sigma}\right]^2\right\} \quad (3)$$

where D_0 and σ are the median and width of the lognormal distribution, respectively, which can be calculated if different moments of the distribution are known, more specifically if the area-weighted crystallite size ($\langle L \rangle_A$) and the volume-weighted crystallite size ($\langle L \rangle_V$) are known. $\langle L \rangle_A$ can be obtained from the Warren-Averbach method, as showed in section 3.2. It is necessary then to calculate the volume-weighted crystallite size. $\langle L \rangle_V$ can also be estimated from the Fourier coefficients

$$\int_0^\infty A^S(L)dL = \frac{\langle L \rangle_V}{2} \quad (4)$$

Assuming a spherical format for the crystallites, it is possible to relate $\langle L \rangle_A$ and $\langle L \rangle_V$ with their diameter.

$$\langle L \rangle_A = \frac{2}{3}D_0 \exp(2.5\ln^2\sigma) \quad (5)$$

$$\langle L \rangle_V = \frac{3}{4}D_0 \exp(3.5\ln^2\sigma) \quad (6)$$

4. RESULTS

According to Eq. 2 the plot of $A^S(L)$ versus L can be used to calculate the area-weighted mean crystallite size ($\langle L \rangle_A$). Fig. 1 shows an example of the final part of the $\langle L \rangle_A$ determination.

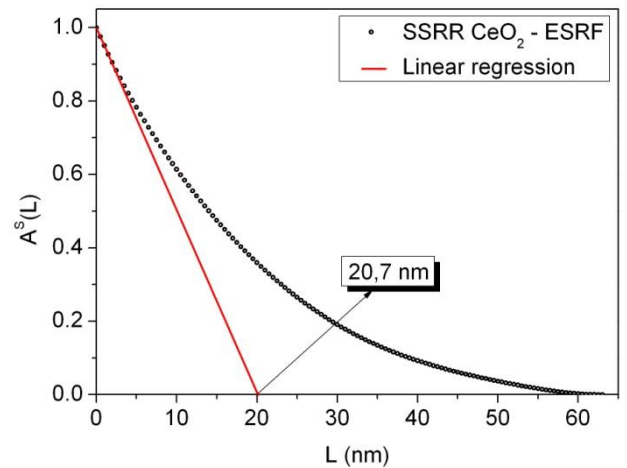


Figure 1: Plot of $A^S(L)$ versus L using the ESRF dataset of the of CeO₂, Round-Robin collective work [4] for the calculation of $\langle L \rangle_A$.

The results for $\langle L \rangle_A$ and RMSS using the Round-Robin data are presented in Tab. 1.

Table 1: Comparison of the results for the $\langle L \rangle_A$ and RMSS.

Dataset	This work		Round-Robin	
	$\langle L \rangle_A$ (nm)	RMSS (10^{-4})	$\langle L \rangle_A$ (nm)	RMSS (10^{-4})
Birmingham	20.5	0.02	17.7	4.4
Le Mans	18.8	0 *	19.8	6.6
ESRF	20.7	0 *	19.5	0 *
NLS	19.9	0 *	19.6	4.1
ILL	21.1	0 *	18.8	4.5
NIST	20.9	0 *	19.4	7.1

In Tab. 1 are presented $\langle L \rangle_A$ and RMSS values for this work and the Round-Robin data. In order to allow a direct comparison, the average values for $\langle L \rangle_A$ were calculated. For this work it was obtained an average value for $\langle L \rangle_A$ of 20.3 ± 0.9 nm and 19.1 ± 0.8 nm for the Round-Robin results considering the results applying the Warren-Averbach method. For the RMSS it was reported in the Round-Robin work [4] that these values are extremely low and can even be neglected.

After the validation of the program the methodology was applied to (101) and (202) reflections of the ZnO samples. The Fourier coefficients related to the size obtained after the separation of the size and strain are shown in Fig. 2.

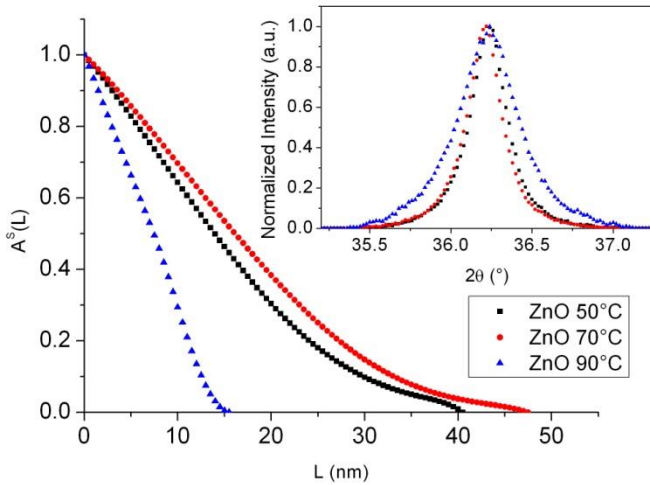


Figure 2: (101) reflection and $A^S(L)$ vs L for the ZnO samples.

The results obtained for $\langle L \rangle_A$, $\langle L \rangle_V$ and RMSS are presented in Tab. 2. A higher value was found for the sample synthesized at 70°C , whereas for the sample synthesized at 90°C the lower value for the $\langle L \rangle_A$ was obtained. And the sample synthesized at 50°C presented $\langle L \rangle_A$ between the two aforementioned values. These results for $\langle L \rangle_A$ are in agreement to those presented in a previous work [5] on the same samples, determined from Rietveld refinements.

In Tab. 2 are also presented the values for $\langle L \rangle_V$. These values are generally higher since its calculation is performed taking into account the volume-weighted size. $\langle L \rangle_V$ values were calculated in order to obtain the crystallite size distributions.

Table 2 – Mean crystallite column-lengths obtained with the Warren-Averbach method.

ZnO	$\langle L \rangle_A$ (nm)	$\langle L \rangle_V$ (nm)	RMSS (10^{-4})
50°C	28.2	41.8	12.4
70°C	32.9	56.2	12.2
90°C	14.8	17.2	27.2

The crystallite size distributions considering a spherical morphology were calculated using the values for $\langle L \rangle_A$ and $\langle L \rangle_V$ presented in Tab. 2. These distributions are also very similar to those obtained by TEM observations presented in that work [5].

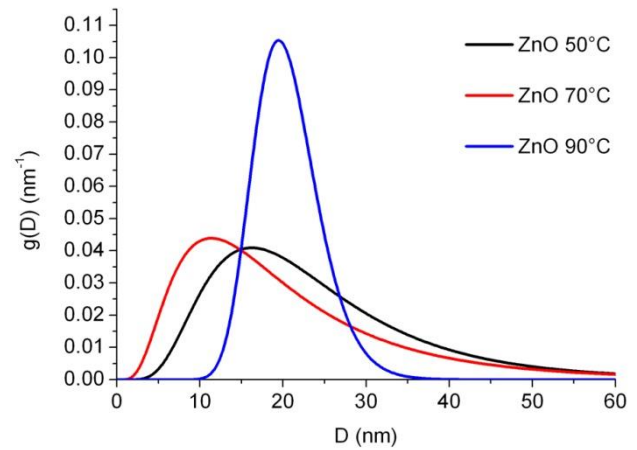


Figure 3: Crystallite size distributions for the 3 samples of ZnO considering a spherical morphology and a lognormal distribution.

Although in this case the results for distribution were in agreement, it is worth to emphasize that TEM images allows observing only few crystallites while distributions determined by XRD methods are based on a great number of crystallites and, consequently, are statistically more representative.

5. CONCLUSIONS

The software developed to apply the Warren-Averbach method was successfully validated when applied to measurements gathered in a Round-Robin collective work, where similar results were obtained.

The application of the methodology carried out on nanostructured ZnO samples provided reliable results for mean crystallites sizes confirming results of Rietveld refinements reported in a previous work on the same samples. Finally, the mean crystallites sizes obtained with the methodology combined with a model for spherical crystallites provided reliable results of crystallite size distributions, as evidenced by the agreement with TEM observations.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

[1] J. L. Gomes, O. Tigli, J.Mater. Sci., 48 (2013), p. 612.

- [2] D. G. Brubaker, M. L. Fuller, *J. Appl. Phys.*, 16 (1945), p. 128.
- [3] B. E. Warren, B. L. Averbach, *B. L. J. Appl. Phys.* 21 (1950) 595–599.
- [4] D. Balzar, N. Audebrand, M. R. Daymond, A. Fitch, A. Hewat, J. I. Langford, A. Le Bail, D. Louër, O. Masson, C. N. McCowan, N. C. Popa, P. W. Stephens, B. H. J. Toby, *J. Appl. Cryst.*, 37 (2004) p. 911.
- [5] M. Gusatti, C. E. M. Campos, D. A. R. Souza, N. C. Kuhnen, H. G. Riella, and P. S. Pizani, *J. Nanosci. Nanotechnol.*, 12 (2012), p. 7986.
- [6] A. S. Galvão, M.Sc. Dissertation, University of São Paulo, São Paulo, Brazil (2011).
- [7] L. G. Martinez, A. S. A. Galvão, J. L. Rossi, M. T. D. Orlando, H. P. S. Correa, and X. Turrillas, in 2010 LMLS Activity Report, Campinas, Brazil, p.126.
- [8] A. Savitzki, M. Golay, *Anal. Chem.*, 36 (1964), p. 1627.
- [9] L. G. Martinez, M.Sc. Dissertation, University of São Paulo, São Paulo, Brazil (1989).
- [10] R. U. Ichikawa, M.Sc. Dissertation, University of São Paulo, São Paulo, Brazil (2013).
- [11] B. D. Cullity, S. R. Stock, *Elements of X-ray Diffraction*, 3rd Ed., Prentice Hall, 2001.
- [12] A. R. Stokes, *Proc. Phys. Soc.* 61 (1948), p. 382.
- [8] C. E. Krill and R. Birringer, *Philos. Mag.*, 77 (1998), p. 621.